# Argonne National Laboratory

MASS-SPECTROMETRIC EFFUSION STUDY
OF URANIUM MONOPHOSPHIDE

by

J. W. Reishus, G. E. Gundersen, P. M. Danielson, and R. K. Edwards The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

# MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University
The University of Iowa

Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame

The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
University of Texas
Washington University
Wayne State University
The University of Wisconsin

#### LEGAL NOTICE -

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

### ARGONNE NATIONAL LABORATORY 9700 South Cass Avenue Argonne, Illinois 60439

# MASS-SPECTROMETRIC EFFUSION STUDY OF URANIUM MONOPHOSPHIDE

by

J. W. Reishus, G. E. Gundersen, P. M. Danielson, and R. K. Edwards

Chemical Engineering Division

November 1968



# TABLE OF CONTENTS

		Page
ABS	STRACT	4
I.	INTRODUCTION	4
II.	EXPERIMENTAL METHODS	6
III.	EXPERIMENTAL RESULTS	7
IV.	THERMODYNAMIC EVALUATIONS	11
	A. Direct Calculation of the Enthalpy of Vaporization and Sublimation of Uranium	11
	B. Indirect Calculation of the Enthalpy of Sublimation of Uranium	13
	C. Calculation of a Value for the Enthalpy of Formation of ${\rm UP}_{1.00}(s)$	14
v.	DISCUSSION	15
AC	KNOWLEDGMENTS	16
RE	FERENCES	17

TABLE OF CONTENTS

.

#### LIST OF FIGURES

No.	Title	Page	
1.	Mass-spectrometrically Determined Partial Pressures of $U(g)$ , $P(g)$ , and $P_2(g)$ over the U-UP System	10	
2.	The P/U Atom Ratio as a Function of Temperature Effusing from a Knudsen Cell Containing U-UP System	10	
	TABLE		
No.	Title	Page	
I.	Third-law Determinations of the Enthalpy of Sublimation of Uranium at 298°C.	11	

A value too the enterior or rubble particles in the second

STREET OF STATE OF STATE

STREET

Maps - spectromistrically Descripted Partial Presences of Utcl. P(g), and P<sub>2</sub>(g) over the G-Ut-System

The P/U Atom Ratio as a Eunction of Temperature Effusing from a Knudsen Cell Containing U-UP System

TITEA

Third-law Determinations of the Enthalpy of Sublumation,

# MASS-SPECTROMETRIC EFFUSION STUDY OF URANIUM MONOPHOSPHIDE

by

J. W. Reishus, G. E. Gundersen, P. M. Danielson, and R. K. Edwards

#### ABSTRACT

A mass-spectrometric effusion study of the vaporization of uranium monophosphide has been completed. Between 2073 and 2423°K, the monophosphide does not vaporize congruently, but instead loses phosphorus preferentially, forming the two-phase system,  $U(\ell)$ -UP<sub>1-x</sub>(s). The vapor species observed were U(g), P(g), and  $P_2(g)$ . The temperature dependencies of the partial pressures in atmospheres are given by

$$\log P_{U} = (5.677 \pm 0.273) - (25898 \pm 192)/T,$$
  
 $\log P_{P} = (8.062 \pm 0.240) - (31831 \pm 340)/T,$ 

and

$$\log P_{P_2} = (10.319 \pm 1.203) - (38454 \pm 1480)/T.$$

A value for the enthalpy of sublimation of uranium at  $298^{\circ}$ K was found to be  $129.0 \pm 3.7$  kcal/mole from averaging our second- and third-law values, which were in good agreement with each other.

#### I. INTRODUCTION

A mass-spectrometric Knudsen effusion investigation of uranium monophosphide (UP) has been carried out in the range 2073-2423°K. Since the monophosphide preferentially vaporized phosphorus and formed the two-phase system  $U(\ell)-UP_{1-\mathbf{x}}(s)$ , the basic thermodynamic properties reported in this report are the partial pressures in equilibrium with this two-phase system.

Uranium monophosphide has a potential as a nuclear fuel, and its stability at high temperatures has been demonstrated in several studies, particularly in the first of two reported mass-spectrometric effusion studies by Gingerich and Lee. 1,2 However, Ref. 1 appears inconclusive for the

MASS SPECTROMETRIC EFFUSION STUDY

vel.

W. W. Beishus, C. E. Gundersen, F. M. Benielson, and R. K. Edwards

### ABSTRACT

A TREAD of the vapor trometrue effection such of the vapor reation of translate above completed. He twees 2073 and 2823°K, the monophosphics does not vapor congruently, but instead, loses provonorus preferentially, formula, the two-channels, who translated the two-channels, preferentially, specific the two-channels, the two-channels are described to the darital pressures in atmospheres are given by

log Py = (5.677 ± 0.273) - (25898 ± 192)/T

bas

log Pp. = (10 319 ± 1 203) - (38454 ± 1480) 1

A value for the outlisty of sublimation of uranium at 296 K was found to be 129.0 ± 3.7 test mole from averaging our second and three-law values, which were in good agreement with each other.

## L INTRODUCIEDN

A mass-spect complete Knudson afficion investigation of granum muscophosphile (UP) has been carried out in the range 2073-242FK. Since the musophosphile preferentially vaporized phosphorus and formed the two-phose system USA-UP-ESS the basic thermodynamic properties reported in this report are the partial presignes in equilibrium with this two-phase existen.

Uranium monophosphide has, a potential as a nuclear fuel, sholds, stability at high temperatures has been demonstrated in several envites, particularly in the first of two reports mask-spectrometric observed by Gingerich and Lee. 12 However, hel drappears inconclusive for the

following reasons: First, although Gingerich and Lee report that the major ion species observed were U<sup>+</sup>, P<sup>+</sup>, and P<sub>2</sub><sup>+</sup>, the phosphorus monomer-to-dimer ratio values they found were inconsistent with those calculated for the P<sub>2</sub> = 2P equilibrium from well-established dissociation energy data. The authors themselves suggest that the discrepancy is likely due to temperature gradients within their effusion cells. Second, although Gingerich and Lee report "...it appears that UP vaporizes congruently over the temperature range of investigation...," they imply that the vaporization becomes incongruent over 2400°K with the formation of a liquid uranium phase. They also suggest that this may occur at lower temperatures, in view of observed evidence that the UP phase tended to deviate from stoichiometry.

More recent work in the literature has confirmed that uranium monophosphide becomes hypostoichiometric on vaporization in vacuum, and there is some concrete evidence that strongly implies that it shifts continuously toward more uranium-rich compositions, finally precipitating out the liquiduranium phase. Thus, Baskin³ has reported the preferential vaporization of phosphorus in vacuum between 1673 and 2473°K and found that the product was hypostoichiometric. Allbutt et al.⁴ reported that vacuum sintering of the monophosphide above 2073°K led to a preferential loss of phosphorus and the formation of a liquid-uranium phase.

Third, although Gingerich and Lee, in treating their vapor-pressure data, adopted the assumption that UP vaporized congruently over the temperature range of investigation, their partial-pressure data argue against the validity of the assumption when the data are used to calculate the composition of the gas phase. Thus, at ~2000°K, Gingerich and Lee report equal partial pressures for the U and P species and approximately one-fourth these values for the P2 species. By appropriately combining the effusion equations, one can calculate that, using their pressures, the composition of the effusing gas in P/U atom ratio units would have been ~3.8. Quite obviously, the solid phase would be in the process of becoming uranium-rich during their measurements. Since the hypostoichiometric range appears to be small (0.00 to ~0.04 unit of x in UP1-x at about 2173°K), vaporization would probably soon lead to rejection of the liquid-uranium phase. Gingerich and Leel noted the tendency toward deviation from stoichiometry, as evidenced by " ... a slight decrease in total vapor pressure and in the Pp/Pu ratio as vaporization proceeded ... . " They did not observe the presence of a uranium phase in the residues that were examined, however.

The present mass-spectrometric effusion investigation was undertaken to resolve some of the conflicts in the accumulated data so that more confidence can be placed on the thermodynamics and stability evaluations of uranium monophosphide.

following reasons: Then, ambruph Gingorica and her report distribe major for species obgained were Ut. 1st., and P. 1 the phosphorius monomerate dimer ratio values they round mean in conservatively there excluding description from the P. 4 LP equilibrium from well introduced distribution spergy details a choice absence in sicoly dec. 1s top-perature gradients within their distribution decreption of the remember the report T. It appears that UP reprises congruently over the remperature range of investigation of their input into the venture of the remperature range of investigation of their input of the remperature over 1sp0" K with the investigation of a liquid uranium plane. They also suggest that the free devices of a liquid uranium plane. They also suggest that UP phase tweeters is experienced, in view of observed excellence that the UP phase tweeters deviced in an acciding out.

More recent work in the interesting continued that urabined more pleased that urabined more pleased that becomes hypoxinchlomateic de vagorvantes in vacent, and there is some teneral more that attough integies that it shifts continuedly for a season of the recent more recent and the respectation of the respectation of the properties and reverse places of the properties and the respectation of the properties and the respectation of the properties and the respectation of the properties and the response of the properties and the response and the response and the properties and the pro

Third, although Guigetob and tare, in treating their, vagor-pressured data, adopted the assumption that the vagorierd congressing court ranger at a present to the sample of the assumption when the data of the validation of the sample of the

the present mess-spectromaters almost investigation may underbless to resolve some of the conflicts in the accumulated data shellon more conflicence can be placed on the thermodynamics and attitudity avaluations of transum monophosphide.

#### II. EXPERIMENTAL METHODS

The mass spectrometer used in this research was a Bendix Model 12-107 time-of-flight instrument operated in the pulsed mode. In this mode of operation, the sensitivity of the instrument is approximately  $10^{-9}$  atm. The practical working mass resolution of the instrument for parent ion species is approximately 1 in 250. The studies were performed using tungsten Knudsen cells, with orifice areas  $(8.1 \text{ or } 2.0) \times 10^{-3} \text{ cm}^2$ , heated by electron bombardment in a high-temperature effusion assembly modeled after that by Rauh et al.  $^7$ 

Temperatures were read with a Leeds and Northrup disappearing-filament optical pyrometer by sighting directly into the orifice of the effusion cell and correcting for the absorbence of the sight glass on the mass spectrometer. The pyrometer filament current was calibrated at the freezing point of pyrometric-standard copper. The calibration of the pyrometer scales at higher temperatures was achieved with tungsten strip bulbs standardized by the National Bureau of Standards. In addition, the pyrometer was compared with another pyrometer which had been calibrated by the rotating-sector method. This comparison showed agreement between the two pyrometers to within 1° at the melting point of platinum.

The uranium monophosphide used was prepared by Baskin and Shalek. Chemical analyses of the material, following the procedures by Milner et al., showed 88.04% uranium (theoretical: 88.49%), 11.30% phosphorus (theoretical: 11.51%), and 0.27% oxygen. Based on these analyses, the P/U atom ratio of the material was 0.98  $\pm$  0.02. Metallographic analysis showed that the oxygen impurity was present as trace amounts of a UO2 phase. A careful search yielded no evidence of a uranium metal phase. X-ray analysis indicated only UP with a lattice parameter of  $a_0 = 5.589 \pm 0.001 \, \text{Å}.$ 

Tungsten was chosen as the container material for the effusion studies, since the available evidence indicated it remained essentially inert to uranium monophosphide up to  $2473^{\circ}\mathrm{K.}^{10}$ 

When stoichiometric uranium monophosphide was initially heated to between 2073 and 2423°K, the ion species observed mass-spectrometrically (using an ionizing electron energy of 30 eV) were  $U^+,\, P^+,\, P_2^+,\, P_4^+,\, UO^+,\, and\, UO_2^+.$  The UP+ species reported in the most recent work of Gingerich² was not observed because the intensity of the ion was below the sensitivity limit of our mass spectrometer. The UO(g) and UO2(g) species arose from the oxygen contamination of the starting material. A survey of the top of the Knudsen cell and the adjoining heat shields, by means of a movable shutter, showed that essentially all the U(g) came from the orifice, but that all the  $P_4(g)$  and part of the  $P_2(g)$  and P(g) arose from revaporization (at relatively low temperatures) of phosphorus which had condensed on heat shields above the effusion cell. Thus, in the first case, there was no cause to suspect that

The mass spectrometer used to this research was a Bendix Medel 12-107 time of flight inchrument operated in the pulsed mode. In the riods of operation, the seasily try of the instrument is appreximately 100% atm. The practical working mass resolution of the matrument for partial ion appetion is appreximately 1 to 200. The studies were performed using stageter Knudsconcells, with orthice areas (8: L or 2: 0) x 10° cm. pasted by electron bombardment in a high-temporature efficient after that by Kauh at a high-temporature efficient assembly

Temporarous were read with a Levils and Northing disappleating disappleating disappleating disappleating disappleating disappleating described and the significant correcting for the absorbence of the significant of the mana space trompers. The production of the freezence point of pyrometric standard copper. The calculation of the pyrometer standards at interesting to the Mattonal Bureau of Standards, in addition, the pyrometer was compared by the Mattonal Bureau of Standards, in addition, the pyrometer was compared by the Mattonal Bureau of Standards, in addition, the pyrometer was compared by the Mattonal Bureau of Standards, in addition, the pyrometer was compared by the Mattonal Bureau of Standards, in addition, the pyrometer was received with another pyrometer which he was a series to write a state matting point of platform.

The uranium money capitide used was prepared by Barkin and Fastelek. Chemical mainteness of the inaterial, following the procedures by Milmer of al., showed 88.04% uranium (theoretical: 88.49%), 11.30% phosphurus (theoretical: 88.49%), 11.30% phosphurus (theoretical: 88.49%), 11.30% phosphurus phorus (theoretical: 88.49%), 11.30% phosphurus the P/U atom ratio of the material was 0.98 to 0.02. Netallographic applications at the original impurity was present as trace amounts of a Ufficience A careful search righted or evidence of a uranium metal phase. X ray analyses multicated only till with a lattice parameter of ap = 5.58 to 0.000 A.

Tungstan was chosen as the containor material for the effurior studies, whose the available evidence (norganizate in remained essentially inert to drawing monophosphide up to 24 TFTs.

When stolchiomeric previous managements was instally peace to between 1073 and 1443°C, the ion species observed mass-spectrometrically (series an nomining all control energy of 30 eV) were Ut. 10. 12. 12. 100°C, and UC. The UT species infinited in the most recently very of Gargerich was not observed because the intensity of the non-very below the sensitivity limit of our mass spectrometer. The UC(s) and 100(s) species areas in the stating material. As an every of the row of the southern cell and the adjoining heat skieleds, by means if a movable entirer showed that essentially all the U(s) come from the briller, but that all the U(s) came from the briller, but that all the U(s) areas from the briller, but that all the live temperatures) of phosphorus which had condensed to best shirt do above the briller on that the briller of the short of the briller of the briller of the briller of the short of the briller of the briller

uranium was "creeping" out of the cell to give enhanced volatilization, and in the second case, background corrections were applied to the observed ion intensities of  $P^+$  and  $P_2^+$  for the secondary vaporization of phosphorus.

An investigation of the dependence of the intensities of U<sup>+</sup>, P<sup>+</sup>, and  $P_2^+$  with the ionizing electron energy showed that all three species were parent species. Appearance potentials were evaluated by the linear-extrapolation method using mercury to calibrate the ionizing-electron voltage scale. Values for the three species were determined to be  $4.7 \pm 0.5$ ,  $10.9 \pm 0.5$ , and  $10.3 \pm 0.5$  eV, respectively. Previous values reported for the appearance potential of U(g) have ranged from 4.7 to 6.25 eV,  $^{11-15}$  and for P(g), 10.977 eV.  $^{16}$  Fragmentation of the  $P_4$ (g) and  $P_2$ (g) species was found to become quite prominent (contributing perhaps 50% of the  $P^+$  observed) at ionizing-electron energies above 18 eV. To avoid this fragmentation, an electron energy of 13 eV was normally used in our experiments.

When a 1-g sample of starting material was heated at 2309°K in 3-hr intervals for 15 hr, the ion intensities of U<sup>+</sup>, P<sup>+</sup>, and P<sub>2</sub><sup>+</sup> became constant after 8 hr at temperature. During this 8-hr period, the partial pressure of U(g) increased by a factor of two and the partial pressures of P(g) and P<sub>2</sub>(g) decreased by factors of two and four, respectively. The partial pressures of UO(g) and UO<sub>2</sub>(g) decreased by factors of 25 and 200, respectively, demonstrating the preferential vaporization of the UO<sub>2</sub> impurity, as was reported by Baskin.<sup>17</sup> As a general procedure, therefore, to clean up the starting material, all samples were given a preheat treatment in the mass spectrometer until the ion intensity ratio of U<sup>+</sup>/UO<sup>+</sup> was  $\geq$ 30. (Typically, this required 1 hr at 2373°K for a 0.2-0.4-g sample.)

#### III. EXPERIMENTAL RESULTS

The observed increase in the partial pressure of U(g) and concomitant decrease in the partial pressures of P(g) and  $P_2(g)$  during effusion in the run discussed above agrees with the observation of Gingerich and Lee<sup>1</sup> and is evidence that the monophosphide phase was tending to become richer in uranium and, therefore, tending to become hypostoichiometric with respect to phosphorus. That the composition of the solid had changed was confirmed by metallographic analysis of portions of the residues from each successive 3-hr heating period. The analysis of quenched\* samples after the 3- and 6-hr periods at temperature revealed UP as the major phase, with  $UO_2$  as a minor phase. After 9 hr at temperature, analyses revealed the presence of uranium as an additional minor phase, located at the UP grain boundaries. The nonuniformity of the distribution of the uranium around the grain boundaries indicated that the uranium existed as a second phase at temperature. Considering the quench rate of the samples, had the uranium precipitated

<sup>\*</sup>Cooled by turning off the power to the electron-emitting filament, cooling from 2270 to 1073°K in 1 min.

uranium was "crooping" out of the cell to give aphanced volatifization, and in the second case, background corrections were applied to the observed inclinations of P\* and Pr\* for the secondary vaporization of phosphorus.

In investigation of the dependance of the intensities of the province of the province of the containst electron energy showed that all three species were parent species. Appearance primitials were evaluated by the imparance parent energy of a species were determined to be \$3.0 a voltage scale. Values for the three species were determined to be \$3.0 a \$1.0 a \$2.0 a

When a log sample of starting material was heated at 1309 M. in the intervals for 15 m. the ion intensities of Ut. 2t. and P. became consists that 8 he is at temperature. During this 8-be period, the partial pressures of P(g) and P(g) increased by a tactors of two and the partial pressures of P(g) and P(g) decreased by factors of the partial pressures of UC(g) and UC(g) and UC(g) and UC(g) decreased by factors of the UC, impurity, as threw distributed by Basical As a general preceders, therefore to clean up the factors were given a probability material in the consisting material, all wrapics were given a probability was 10. Topically, this tentum in the mass approximation in the mass approximation of the ion intensity ratio of UP(UC) was 10.

# THE EXPERIMENTAL RESULTS

The observed intrease in the partial pressure of U(g) and concomitant decrease in the partial pressures of F(g) and F, g) antify efficient in the year discussed above agrees with the observation of the gerich and the complete with the monophosphide phase was tending to become richer in the manufacture tending to become hypostotichiometric with respect to prophoson. That the composition of the solid had changed was confirmed by metallogisphic analysis of portions of the residues from each successive by metallogisphic analysis of portions of the residues from each successive for particle at temperature respected UP as the monophase, with UO, as a minor phase. After 7 hr at temperature, analyses revealed the presence of uranium as an additional minor phase, located at the UP grain boundaries of uranium as an additional minor phase, located at a second phase at temperature arise malested that the uranium existed at a second phase at temperature arise malesting the quench rate of the samples, but the uranium precipitated as a second ghase at temperature

Couled by received by received off the power to the electron-endicing themen, evelog figure 27% to 1072-Y. is 1 men.

from hypostoichiometric uranium phosphide upon cooling, it would probably have been more uniformly distributed around the UP grains. This nonuniformity in the distribution of the uranium phase among the UP grain boundaries was also observed by Allbutt et al. and cited as evidence for the presence of liquid uranium at temperature. It was also noted in our metallographs that the uranium phase of the quenched samples contained 5-11 wt tungsten. The authors of Ref. 18 found the solubility of tungsten in liquid uranium to be 5.8 at. at 2273 K, corresponding to 7.5 wt tungsten.

X-ray diffraction analyses of quenched\* samples following vaporization showed that the lattice parameter of the UP was always unchanged from its original value of  $a_0 = 5.589 \pm 0.001$  Å. This disagrees with the results of Baskin,³ who found a decrease in the parameter from  $a_0 = 5.589$  Å to 5.583 Å, as the stoichiometry of the monophosphide decreased from 1.00 to 0.97. The reason for this disagreement, at present unknown, appears to be complex, possibly involving different cooling rates, effects of tungsten impurities, and/or the physical state (powder or pellet) of the starting material.

The partial vapor pressures of U(g), P(g), and P2(g) over the twophase system  $U(\ell)$ - $UP_{1-Y}(s)$  were determined as a function of temperature from measurements of the U<sup>+</sup>, P<sup>+</sup>, and P<sub>2</sub><sup>+</sup> ion currents in four separate experiments. The calibration to convert ion intensities to partial pressures was obtained by the rate-of-mass-loss method. That the condensed materials in these experiments did correspond to the two-phase system was determined metallographically or mass-spectrometrically. The latter was accomplished by heating a disk of starting material at a constant temperature until the intensities of the three ionic species were constant with time, and then adding a small pellet of uranium to the disk and again heating to the same temperature. The intensity of the U+ species was equal to its intensity observed before the uranium charge had been added and did not vary with time. This equivalency established that, during effusion, the starting material had indeed shifted composition to become the two-phase system even before addition of the uranium pellet. The P/U atom ratio of the solid was initially  $0.98 \pm 0.02$  and  $0.95 \pm 0.02$  at the end of the experiment, as determined by chemical analysis. Since excess uranium was present in the residue, the ratio  $r_s$  at the phase boundary is  $0.98 > r_s > 0.95$ , or approximately 0.965 ± 0.02, which compares well with the 0.96 value at 2137°K, as communicated to us by Bowman.5

The partial pressure of an effusing species,  $P_i$ , is related to its ion current,  $I_i$ , and its mass rate of Knudsen effusion,  $Q_i$ , by

$$I_{i}T = C_{\sigma_{i}\gamma_{i}}P_{i} = C_{\sigma_{i}\gamma_{i}}Q_{i}\sqrt{\frac{2\pi RT}{M_{i}}}, \qquad (1)$$

<sup>\*</sup>Ibid., see p. 7.

from hyposteichlometric uranium prespinte upon mobilog, it would probably have been more uniformly distributed around the the grains. Thus become formuly in the distribution of the uranium phase among the UE grain boundaries was also observed by Allbart et al." and eited as evidence for the presence of liquid uranium at temperature. It was also noted in our metallog graphs that the uranium phase of the quenched samples contained 5-11 with ungates. It (The authors of East 13 found the solidility of tungsten in liquid uranium to be 5-8 at \$1275 K, corresponding to 7 5 we W tungsten.)

E-ray diffraction analyses of quanched, samples following superiesation showed that the lattice parameter of the UP was always unchanged from its original value of as 5.589 ± 0.001 Å. This disagrees with the results of Daskin, who found a decrease in the parameter from as = 5.589 Å to 5.583 Å, as the statchiometry of the manophosphide decreased from 1.00 to 0.97 The research for this disagreement at present unknown, appears to be complex, possibly involving different cooling rates, effects of nangeled integurities, and/or the payerral state (porder or pellet) of the starting material purities, and/or the payerral state (porder or pellet) of the starting material

The partial vapor pressures of U(g). P(g) and P.(g) over the year phases system U(g)-UP(-x(s) was determined sets income of temperature at them measurements of the U. P. and P. tem currents to four separate sequentiments. The calibration to convert non-intensities to satisfar pressures was obtained by the rate of suras-loss ungelled. I get the condensed material resembled by the rate of unass-spectrometrically. The latter was remined metallographically or mass-spectrometrically. The latter was remined the intensities of the startine insterial as accommon unpersonal intensities of the three cometrics are closes and again heating to the fact them added the adding a small paget of prantiments of the Uffice of the control of the meaning to the observed before the unanimeters of the Uffice of added and did not the parents that the observed before addition of the unanimeters had be only at the end of the competition of the unanimeters and the competition of the unanimeters and the competition of the control of the co

The partial presence of an educing species, I, is related to he four currentity and its measurement of the control of the second of the second

Mr - Compt - Comot V M

on a see

where T is the absolute temperature, C is a constant characteristic of the electronics and geometry of the mass spectrometer, o; is the ionization cross section,  $\gamma_i$  is the multiplier efficiency, and  $M_i$  is the molecular weight. The partial pressures were evaluated 19 from three measurements at a constant temperature (2309°K) of the total mass evaporated in a given time and the intensity of each main ion species integrated as a function of time. Then the observed total mass rate of effusion, Q<sub>T</sub>, was partitioned into that due to each of the three principal species by use of the ratios of Eq. 1 with the necessary coefficients estimated as follows. Otvos-Stevenson<sup>20</sup> ionization cross sections were used ( $\sigma_{II}$  = 55.7,  $\sigma_{P}$  = 13.8, and  $\sigma_{P}$ , = 27.6), and multiplier efficiencies were estimated on the assumption<sup>22</sup> that ions of equal velocity have equal multiplier efficiencies; i.e.,  $\gamma_1/\gamma_2 = (M_2/M_1)^{1/2}$ , where M is the molecular weight. When it was necessary to correct evaporation rates for the presence of UO(g) and  $UO_2(g)$ , the assumption that  $\sigma_{II} = \sigma_{IIO} =$  $\sigma_{\mathrm{UO_2}}$  was used. This assumption was evaluated to be satisfactory in the studies on the U-UO<sub>2</sub> system.<sup>22</sup> From the three measurements of the rate of mass loss at 2309°K from the  $U(\ell)$ - $UP_{1-x}(s)$  system, the average weight loss through an orifice of 0.101-cm diameter was at the rate of 2.02 mg/ (min)(cm2). Since a linear extrapolation to this temperature of the data obtained between 1823 and 2174°K from the Langmuir evaporation experiments by Allbutt et al.4 gave an evaporation rate that was within a factor of two (higher) of our value, there appears to be no indication for a vaporization coefficient significantly different from unity.

The partial pressures of U(g), P(g), and  $P_2(g)$  were calculated to be  $2.89 \times 10^{-6}$ ,  $1.89 \times 10^{-6}$ , and  $4.62 \times 10^{-7}$  atm, respectively, at  $2309^{\circ}K$ . The equations for the temperature dependencies of the three partial pressures in atmospheres are

$$\log P_{U} = (5.677 \pm 0.273) - (25898 \pm 192)/T,$$
 (2)

$$\log P_{\mathbf{P}} = (8.062 \pm 0.240) - (31831 \pm 340)/T,$$
 (3)

and

$$\log P_{\mathbf{P}_2} = (10.319 \pm 1.203) - (38454 \pm 1480)/T$$
 (4)

from the four series of ion-current measurements, mentioned previously, which had been combined by normalizing the data to a common basis at the midrange temperature. These equations are considered valid in the range  $2073-2423^{\circ}K$ . From the uncertainty in the experimental data alone, the partial pressures of U(g), P(g), and  $P_2(g)$  are known (at a 95% confidence level,  $2\sigma$ ) to within 18, 20, and 44%, respectively. However, it is generally assumed that uncertainties in the ionization cross sections and multiplier efficiencies could be a factor of two. Figure 1 shows the lines representing the above pressure equations, one set of the experimental data (the uranium data is given in Table I, Series A), and, for comparison, the equations reported by Gingerich and Lee<sup>1</sup> from their similar mass-spectrometric

where T is the absolute temperature. C is a constant characteristic of the electronics and geometry of the mass spectrometer, 0; is the temperature reasons settleton, 3; is the molecular weight. The partial pressures were evaluated from three measurements at a constant fumperature (2300°X) of the total mass evaporated in a given time and the interestry of each roain ion species integrated as a function of time. Then the interestry of sach roain ion species integrated as a function of time. Then the three principal species by use of the ratios of i.q. I with the necessary coefficients astimated as follows. Onvok-Stevenson contaction of the climated as follows. Onvok-Stevenson contaction of the climated as follows. Onvok-Stevenson contaction of the ration were estimated as follows. Onvok-Stevenson contaction with the prior equal multiplier efficiencies were estimated on the assumption that of equal wis the molecular weight. When it was presently to correct evaporation as the molecular weight. When it was presently to correct evaporation of mass for the presence of UO(2) and UO(2), the exercise to the rate of the presence of the UO(2) and UO(2) are measured on that of one rate of masselons at 2,00°K from the UO(2) are measured equals to the rate of masselons at 2,00°K from the U(2)-UP(2-x) system the sweater attended to the case of the data data data through an orifice of 0 (0)-cm aismeter was at the rate of 2.02 mg/min)(cm \*\* Since a linear extrapolation to the consecutive of the data.

The partial presence of U(g), P(g), and P(g) were excepted to be 3.89 x 10 %, and 4.62 x 10 % and 1.62 x 10 % atmospheres are

tog Pg = (5.677 ± 0.273) - (25898 ± 192)/T)

10g Pu = (8.062 ± 0.240) - (31831 ± 340)/T

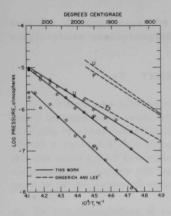
one

log Per = (10.319 ± 1.203) - (38454 t 1480)/1

From the four series of ion-current measurements, mentioned previously, when not been combined by normalizing the data to a common basis at the midrange temperature. These equations are considered wild in the range 2073-2423°K. From the uncertainty is the experimental data along the partial pressures of U(g), F(g), and F<sub>2</sub>(g) are known (,a g 35° continues level, 20) to within 18, 20, and 44%, respectively. However, it is contraint assumed that uncertainties in the ionization cross sections and multiplier efficiencies could be a factor of two. Figure 1 above the lines representing the above pressure equations, one actor the experimental data (10 treatment data is given in Table I. Series A), and, for compartson the equation requestion ported by Gingerich and Lee' from their similar measuremental content of the content of the compartson the equation reconstruction of the content of the content

ered by Jungerica son

teed by Gingerice and



308-1032 Rev. 1

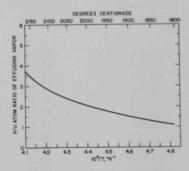
Fig. 1. Mass-spectrometrically Determined Partial Pressures of U(g),
P(g), and P<sub>2</sub>(g) over the U-UP
System

effusion experiments. There is considerable disagreement between their absolute pressures and enthalpies of vaporization and ours. Their partial pressures are approximately an order of magnitude greater than our corresponding pressures. The apparent enthalpies of vaporization that we derive from their vaporpressure equations (Eqs. 5, 6, and 7 of Ref. 1) are  $\overline{\Delta H}(U) = 131.2 \text{ kcal/mole}, \overline{\Delta H}(P) =$ 120.0 kcal/mole, and  $\overline{\Delta H}(P_2) = 105.5$  kcal/mole, as compared to our values of 118.5, 145.7, and 176.0 kcal/mole from Eqs. 2, 3, and 4, respectively. The internal consistency of our results, as judged by the P2 = 2P equilibrium, was very satisfactory. The Gibbs free energy, enthalpy, and entropy of dissociation of P2(g), calculated from Eqs. 3 and 4 at 2248°K were 55.6 kcal/mole, 115.4 kcal/mole, and 26.6 eu. respectively. From spectroscopic data, 23 the corresponding values are 54.8 kcal/mole, 119.2 kcal/mole, and 28.7 eu. Also, a com-

parison at 2309°K of our partial pressure ratios shows a monomer/dimer ratio of 4.09 from direct measurement (using the estimated cross sections and detector efficiencies), versus 4.90 calculated from inserting the measured monomer pressure into the equilibrium constant<sup>23</sup> expression. As mentioned in the Introduction, Gingerich and Lee's  $P_2 = 2P$  data<sup>1</sup> did not agree with these well-established equilibrium data, <sup>23</sup> and their suggestion that the discord was probably due "...especially to possible temperature gradients in the effusion cell..." could also serve as a possible explanation for the disagreement between our work and theirs. Another possible explanation could be that their vaporization was from a single condensed phase,

in that their  $\mathrm{UP}_{1-\mathrm{X}}$  solid had not changed sufficiently to form the liquid-uranium phase.

The observed change in composition during effusion of stoichiometric uranium monophosphide over to the system of two condensed phases demands that the vapor effusing from the cell be phosphorus-rich. The partial pressure data expressed by Eqs. 2, 3, and 4 are consistent with this requirement. Figure 2 presents the derived atom ratio of the vapor effusing from the two-phase system in the Knudsen cell as a function of temperature. Since the rate of effusion loss of phosphorus substantially exceeds



308-1033

Fig. 2. The P/U Atom Ratio as a Function of Temperature Effusing from a Knudsen Cell Containing U-UP System

elector experiments. There is considerable disagreement between their chackule pressure and entirely en entirely en entirely en enter of representation and outs. Their pressures. The apparent entirelying of vaporable that we derive from their vaporables that we derive from their vaporables that we equations. I can be a seed of other 1) pressures equations. I can be a seed of other 1) pressures equations. I can be a seed of other 1) and a seed out water and a seed out a

results, as sunged by the 10 - in equipment of the control of the

corresponding values are 94.8 kcal/mole, 2019 119 2 kcal/mole, and 25 7 eu. Also, a romaiel pressure ratios above a monomer/dimensiel

alloys and the content of saurement (using the estimated cross sections and detector efficienties), we cause 4.00 calculated from meeting the measure moments present and the content of the measurement of the content of the content

n that their UP, solid hadenot changed ratherings to form the liquid-uranion

ogmos di agnada bevrezde seil de la compo di agnada bevrezde seil de la compo di agnada bevrezde seil de la compo de la compo

Eding to the same

that for uranium over the two-phase system, it must be true for the single-phase monophosphide also.

#### IV. THERMODYNAMIC EVALUATIONS

There are alternate ways of treating our data, depending upon which basic assumptions seem most reliable. One may treat the uranium data directly to obtain an enthalpy of sublimation of uranium. One may also obtain a value for this quantity indirectly by using calorimetric data reported for the enthalpy of formation of UP(s). The third possibility, of course, is to calculate a value for the enthalpy of formation of UP from our data to compare with the reported value. These alternatives are considered below.

# A. Direct Calculation of the Enthalpy of Vaporization and Sublimation of Uranium

If we assume that the liquid uranium of the two-phase system, saturated with UP<sub>1-x<sub>S</sub></sub>(s) and W(s), is at unit activity at all temperatures of the measurements, the partial uranium pressures, expressed by Eq. 2, would represent the true vapor pressure of liquid uranium, and the second-law apparent partial enthalpy,  $118.5 \pm 0.9$  kcal/mole at 2248°K, would be the enthalpy of vaporization of uranium. This value, calculated to 298°K through use of the Hultgren et al. <sup>24</sup> functions, yields  $\Delta H_{298}^2 = 128.3 \pm 1.3$  kcal/mole for the enthalpy of sublimation of uranium. Table I lists the primary log P<sub>II</sub> data and the derived third-law enthalpies of sublimation for the

TABLE I. Third-law Determinations of the Enthalpy of Sublimation of Uranium at 298°C

Temp (°K)	-Log P <sub>U</sub> (atm)	$\Delta G_{\mathrm{T}}^{\circ}$ (kcal/mole)	$-\Delta(G_{\mathrm{T}}^{\circ}-H_{298}^{\circ})^{\mathrm{a}}$ (kcal/mole)	$\Delta H_{298}^{\circ}(U)$ (kcal/mole)
2126		Series A		
2118	6.546	65.21	66.14	131.35
2158	6.262	61.84	67.20	129.04
2223	6.007	61.09	68.87	129.96
2251	5.766	59.39	69.61	129.00
2280	5.689	59.34	70.40	129.74
2307	5.525	58.38	71.15	129.53
2335	5.446	58.16	71.87	130.03
2358	5.294	57.12	72.50	129.62
2390	5.220	57.11	73.35	130.46
2408	5.106	56.27	73.85	130.12
2430	5.002	55.62	74.42	130.04
2430	5.007	55.68	74.42	130.10

that for urantum over the mo-place system, it must be true tor the

# THE EMODYMANIC SVALUATIONS

liers are alternate ways of preating our date depending upon which bears assumptions seem most rethank One may read the practing total date of the contains as antibility of sublimation of practice of the contains a value for the questity indirectly by using cancilmetric data reported for the estimator of UP(s). The third coathing, of course, is in calculate a value for the cathains of Originalism of UP from our data to compare with the reported value. These electronities are considered below.

A. Direct Calculation of the Estactpy of Vaporization and Suitimation of Cyticklane

If we assume that the liquid restricts of the two-phase system; synchroted order UP; e.g.(2) and W.(a), it at our activity at all temperatures of the meaning of most of the expression of the fact of

TABLES. Tifferd-law Determinations of the Enthalpy

	15. A6 A9. 14 / 15 90. 16 91. 66 A1. 66 A1. 66 A3. 86 A3. 86 A5. 86 A5. 86 A	

TABLE I (Contd.)

Temp (°K)	-Log P <sub>U</sub> (atm)	$\Delta G_{\mathrm{T}}^{\circ}$ (kcal/mole)	$-\Delta (G_{\rm T}^{\circ} - H_{298}^{\circ})^{\rm a}$ (kcal/mole)	$\Delta H_{298}^{\circ}(U)$ (kcal/mole)
		Series B		
2112	6.590	63.69	65.97	129.66
2112	6.590	63.69	65.97	129.66
2112	6.596	63.75	65.97	129.72
2146	6.381	62.66	66.87	129.53
2146	6.373	62.58	66.87	129.45
2147	6.394	62.82	66.89	129.71
2178	6.217	61.96	67.70	129.66
2178	6.238	62.17	67.70	129.87
2237	5.868	60.09	69.25	129.34
2237	5.899	60.41	69.25	129.66
2240	5.921	60.69	69.33	130.02
2268	5.746	59.64	70.10	129.74
2268	5.763	59.82	70.10	129.92
2270	5.743	59.67	70.12	129.79
2270	5.759	59.84	70.12	129.96
2344	5.388	57.81	72.10	129.91
2345	5.370	57.62	72.13	129.75
2370	5.194	56.35	72.81	129.16
2370	5.217	56.60	72.81	129.41
		56.67	72.81	129.48
2370	5.223	56.53	72.85	129.38
2372	5.210	56.44	73.09	129.53
2380	5.183	56.58	73.13	129.71
2382	5.191	55.73	73.88	129.61
2410	5.053	56.05	73.88	129.93
2410 2410	5.082 5.044	55.64	73.88	129.52
		Series (		
2126	6.464	62.89	66.35	129.24
2126	6.354	61.82	66.35	128.17
2126	6.514	63.37	66.35	129.72
2229	5.965	60.84	69.05	129.89
2229	5.968	60.87	69.05	129.92
2229	5.947	60.66	69.05	129.71
	5.676	59.31	70.51	129.82
2284	5.670	59.25	70.51	129.76
2284	5.706	59.63	70.51	130.14
2284	5.680	59.36	70.51	129.87
2344	5.342	57.32	72.10	129.42
	5.379	57.72	72.10	129.82
2344	5.359	57.50	72.10	129.60
	5.164	56.49	73.39	129.88
2391	5.169	56.55	73.39	129.94
2391	5.164	56.49	73.39	129.88

	1000	
	56.65	

TABLE I (Contd.)

	(atm)	$\Delta G_{\mathrm{T}}^{\circ}$ (kcal/mole)	$-\Delta (G_{\rm T}^{\circ} - H_{298}^{\circ})^{a}$ (kcal/mole)	$\Delta H_{298}^{\circ}(U)$ (kcal/mole)
	dhie di 1866	Series D		
2073	6.805	64.55	64.94	129.49
2073	6.859	65.06	64.94	130.00
2073	6.793	64.44	64.94	129.38
2145	6.390	62.72	66.85	129.57
2147	6.403	62.91	66.89	129.80
2147	6.370	62.59	66.89	129.48
2148	6.382	62.73	66.92	129.65
2189	6.212	62.24	68.00	130.24
2209	6.049	61.16	68.51	129.67
2209	6.037	61.03	68.51	129.54
2210	6.080	61.47	68.54	130.01
2210	6.041	61.07	68.54	129.61
2210	6.112	61.79	68.54	130.33
2270	5.739	59.63	70.12	129.75
2270	5.733	59.57	70.12	129.69
2270	5.769	59.94	70.12	130.06
2270	5.755	59.79	70.12	129.91
2324	5.482	58.27	71.56	129.83
2326	5.436	57.84	71.65	129.49
2326	5.461	58.11	71.65	129.76
2326	5.461	58.11	71.65	129.76
2326	5.472	58.22	71.65	129.87
2378	5.159	56.13	73.05	129.18
2378	5.166	56.21	73.05	129.26
2389	5.075	55.47	73.32	128.79

 $^{
m a}$ Values taken from a smooth curve drawn through the listed values compiled by Hultgren et  $\overline{
m al}$ . $^{
m 24}$ 

bThis standard deviation reflects the precision. The accuracy of the value is estimated to be ±3.3 kcal/mole.

four series of measurements. The values do not show a temperature trend, and the average value,  $\Delta H_{298}^{\circ}$  = 129.7  $\pm$  3.3 kcal/mole, is in satisfactory agreement with the second-law value. The average of the second- and third-law values is 129.0  $\pm$  3.7 kcal/mole.

# B. Indirect Calculation of the Enthalpy of Sublimation of Uranium

Here, we first assume that the enthalpies derived from Eqs. 2 and 3 are valid partial molar values for any of the compositions  $UP_{1-x_S}$ , where  $x_S$  refers to the uranium saturation boundary. This could be true if  $x_S$  did not vary significantly with temperature or if the partial pressures at each temperature did not vary significantly in the range of variation of  $x_S$ . Then

Values lakes from a smooth curve drawn through the listed values compiled by Holloren et al.

Time standard deviation reflects the practaton. The acciracy of the value is sectioned to be 13.3 healthcale.

four series of measurements, The values do not show a temperature frond, and the everage value, 07%, -129,7 t 7.3 heal/mole, is in satisfactory agreement with the second-law value. The average of the second-out third-law values is 139,0 t 3,7 heal/mole.

## I defrect Categlation of the Enthalpy of Sublimation of Uraniam

Here, we thus assume that the rethelples derived trong Eqs. Send Were walls partial molar values for any of the compositions UP, 37, where a refers to the aradium same aim boundary. This could be true thus thus did not vary significantly with temperature or if the range of variation of x2. Then

it would follow that the "apparent" partial molar enthalpies obtained for the two-phase preparations, from Eqs. 2 and 3, would be valid partial molar quantities and constant in the range of variation of  $x_s$ . A second assumption required regards the variation of these partial molar enthalpies for the range  $x_s$  to x=0. It is assumed that the variation is negligible or that the change in the partial enthalpy for one component compensates for the change in the other component (as they would at least tend to do). Subject to these assumptions, the enthalpy of sublimation of  $UP_{1.00}(s)$  to the monatomic gases is the sum of their partial molar enthalpies of vaporization or  $264.2 \pm 1.8 \text{ kcal/mole}$ . Using this data, one can calculate an enthalpy of sublimation (in kcal/mole) for uranium at  $298^{\circ}\text{K}$  from the following cycle:

The value derived for the enthalpy of sublimation,  $117.2 \pm 3.0 \text{ kcal/mole}$ , is essentially a second-law value.

# C. Calculation of a Value for the Enthalpy of Formation of UP1.00(s)

The most obvious way to calculate an enthalpy of formation from our high-temperature equilibrium data is to use the thermodynamic cycle given above and solve for the enthalpy of formation of UP<sub>1.00</sub> rather than the enthalpy of sublimation of U(g). If one does this, using the average value of our second- and third-law determinations for the enthalpy of sublimation of U(g) at 298°K, 129.0  $\pm$  3.7 kcal/mole, an enthalpy of formation for UP<sub>1.00</sub> at 298°K is calculated to be -63.7  $\pm$  4.4 kcal/mole. A third-law evaluation gives the same result within 1.8 kcal/mole. To eliminate the necessity of using an enthalpy of sublimation for U(g), we could have used a thermodynamic cycle based on our data for the following reaction:

$$U(\ell) + (1 - x) P(g) = UP_{1-x}(s).$$
 (5)

Here we would again assume not only that the liquid uranium of the twophase equilibria is at unit activity in the temperature range of the

<sup>\*</sup>Calculated using the reported mean heat capacity for uranium monophosphide, 13.8 cal/deg/mole, in the range  $1073-1473^{\circ}$ K by Brugger. <sup>25</sup>

It would follow that the "apparent" partial moist enthalpies obtained for the (mo-phase preparations, from Eqs. 2 and 3, would be valid partial molar (mo-phase preparations) and the range of variation of x. A second assumption required regards the variation of these partial molar enthalpies for the range x. fox = 0. It is easymed that the variation's negligible or that the change in the partial ambains for one compensate or that the change in the partial ambains for one compensate of the change in the other-complete in the substitution of UP, e.(s) to the monatomal gaess as most and of the first partial molar enthalpias of range (and or 264.2 for the monatomal gaess is the sum of their partial molar enthalpias of range (and or 264.2 for the monatomal gaess is the sum of their partial molar enthalpias of range (and or 264.2 for the monatomal gaess is the sum of their partial molar enthalpias of range (allowers cycle) the monatomal and the followers cycle) then the call mole that the followers cycle.

The value derived for the enthalpy of sublimation, 117.2 2 3.0 keal/mole, is covered law value.

# C. Calculation of a Value for the Enthalpy of Pormation of CP, m(s)

The most obvious way to calculate an corbally of formation from our bigh-temperature equilibrium data is to dec the the emodynamic cycle given above and solve for the cathalpy of formation of UP; corrather than the enthalpy of explainments of the exercise of the exercise.

Here we would sgain average not only that the liquid evanium of the two

<sup>(</sup>Supplement using the reported mines been appears for transfer enoughopility, LaS cal/or/color) in the reage 1752-1672°K by fingget. In the reage 1752-1672°K by fingget. In

measurements, but also that the activity of  $UP_{1-X}$  is not significantly different from unity over the temperature range of measurements. With these assumptions, the second-law enthalpy of formation for Reaction 5 is simply -145.7 kcal/mole from Eq. 3. If this value is corrected from the midrange temperature, 2248 to 298°K, using the appropriate thermodynamic functions listed in the references given in the cycle above, a value for the enthalpy of formation of  $UP_{1,00}$  identical to the one calculated above is obtained.

#### V. DISCUSSION

Let us first consider our direct calculation of the enthalpy of sublimation of uranium. The question of the correct value for this quantity has recently been reviewed by Ackermann and Rauh, 28 who also present new data concerning the effect of dissolved tantalum, phosphorus, sulfur, carbon, and oxygen on the vapor pressure of liquid uranium. They noted the substantial agreement between our second-law enthalpy of vaporization for uranium over the  $U(\ell)$ - $UP_{1-x}(s)$  system (118.5 ± 0.9 kcal/mole at 2248°K) and their result (115.5 ± 1.7 kcal/mole at 2100°K). They found that uranium phosphide had the smallest effect of any of the compounds on the vapor pressure of uranium and estimated an activity of ~0.9 at 2000°K, which adequately supports our assumption of unit activity in our calculations. Although our uranium partial pressures are in close agreement with those of Pattoret et al., <sup>29</sup> for uranium in a tungsten or tantalum effusion cell  $(2.89 \times 10^{-6} \text{ atm of } 2309^{\circ}\text{K} \text{ compared to their } 4.15 \times 10^{-6} \text{ atm})$ , they are a factor of approximately one-half lower than those obtained by Ackermann and Rauh. 28 The latter authors' suggestion, that our values are low because of the rate-of-mass-loss method of calibration with its usual failure30 to account for nonideal cosine distribution of the effusing molecules, seems reasonable.

Ackermann and Rauh<sup>28</sup> evaluated an enthalpy of sublimation for uranium at 298°K of 126.3  $\pm$  1.0 kcal/mole and compared it with 128.5  $\pm$  2.0 kcal/mole by Pattoret et al.<sup>29</sup> (this value being actually for 0°K) and 123.7  $\pm$  1.3 kcal/mole reported by Leitnaker and Godfrey.<sup>31</sup>

Both our second-law (128.3  $\pm$  1.3) and our third-law (129.7  $\pm$  3.3) values and their average (129.0  $\pm$  3.7) are in excellent agreement with the values reported by Pattoret et al. 29 and Ackermann and Rauh. 28 Our results thus support the long-held contention of the former authors and the more recently expressed view of the latter that the earlier value of Rauh and Thorn, 32 116.6 kcal/mole, is no longer tenable.

Our indirect calculation of the enthalpy of sublimation of uranium, using the enthalpy of formation of UP by O'Hare et al. 27 and yielding a value of 117.2 kcal/mole, points up an inconsistency in this calculation. Likewise,

mosairrments, but also that the activity of UF; at not expained anly different from quity over the temperature range of measurements. With these assumptions, the acconding entirety of formation for Beaston a is simply -143.7 real/mote them, 1, it this value is corrected from the midrange temperature, 2243 to 298 K, using the appropriate themselvannic functions listed in the relevances given in the cycle above, a value for the entirety of formation of UF, or identical to the one calculated above is obtained.

#### V DISCUSSION

in the second problem of the question of the enthalton of the enthalton of the enthalton of creative.

In recently been reviewed by Ackermans and Rauh, who also present new data concerning the effect of the couple tanishum, phosphores, suffer carbon, and expendent between our econdedaw enthalty of reportation and problems are distincted to the couple of the couple

At Resimple and Resilf evaluated an epibelpy giventalized for uranium at 298 K of 126.3 t 1.0 kct//mole and compared it with 125.5 t 2.0 km/mole by Petrores at al. (turn value being actually for C.E.) and 2.3 f 2.1. t kcal/mole reported by Lestinghor and Contray.

Sort our seroid-less (126.3 : 1.2) and opr chird-less (126.7 i.3.1) related and the content of t

Our indicort call classes of the embalgy of exhibitation of meaning of sublimation of meaning as well as the embalgy of force of the contract of the contract

this inconsistency is seen in our value for the enthalpy of formation for UP<sub>1.00</sub> at 298°K of -63.7  $\pm$  4.4 kcal/mole compared to the calorimetric value of -75.5  $\pm$  0.7 kcal/mole of O'Hare et al. Since there seems little reason to suspect the calorimetric value for the enthalpy, doubt is cast on one or both of the assumptions used in our calculations. Most likely one cannot assume that the partial molar enthalpies of vaporization of U(g) and P(g) are constant over the composition range of UP<sub>1-x</sub> to UP<sub>1.00</sub>.

#### ACKNOWLEDGMENTS

We wish to thank Y. Baskin for supplying the uranium monophosphide used in this investigation and A. E. Martin for his aid in the metallographic analysis of samples.

this inconsistency is even to our value for the orthalpy of formation for UF, to at 295 K, of +63.7 & 4.6 Scalymole compared to the caloringetric value of -15.5 & 0.7 keek made of O'liare et al. Since there seems little reason to author the calorimetric value for the enthalpy dools is east on one or both of the examptions used to our calculations. Most fixed one cannot assume that the parties malar enthalpies of vaporisations of U(g) and U(g) are constant over the composition range of U(F), to UK. 36

#### ACTOR DUBLISHED SERVER

We wish to thank f, Heslan far supplying the premium monophosphile used in this investigation and A.E. Martin for his all in the metallographic analysis of samples

#### REFERENCES

- 1. K. A. Gingerich and P. K. Lee, J. Chem. Phys. 40, 3520 (1964).
- 2. K. A. Gingerich, Naturwissenchaften 53, 525 (1966).
- 3. Y. Baskin, J. Am. Ceram. Soc. 49, 541 (1966).
- 4. M. Allbutt, A. R. Junkinson, and R. G. Carney, Atomic Energy Research Establishment Report, AERE-R-4903 (1965).
- 5. M. G. Bowman, Los Alamos Scientific Laboratory (private communication).
- 6. W. C. Wiley and I. H. McLaren, Rev. Sci. Instr. 26, 1150 (1955).
- 7. E. G. Rauh, R. C. Sadler, and R. J. Thorn, High-temperature Knudsen Effusion Cell Assembly, ANL-6536 (April 1962).
- 8. Y. Baskin and P. D. Shalek, J. Inorg. Nucl. Chem. 26, 1679 (1964).
- G. W. C. Milner, D. H. Rowe, and G. Phillips, Atomic Energy Research Establishment Report, AERE-R-4096 (1965).
- Reactor Development Program Progress Report, January 1966, ANL-7152 (Feb. 24, 1966), p. 56.
- E. G. Rauh, Work Function, Ionization Potential, and Emissivity of Uranium, ANL-5534 (May 1956).
- W. A. Chupka, in Physics Division Summary Report, July through September 1957, ANL-5786 (Nov 1957), p. 75.
- J. R. Werning, University of California Radiation Laboratory Report, UCRL-8455 (1958).
- 14. J. B. Mann, J. Chem. Phys. 40, 1632 (1964).
- 15. C. R. Hertel, J. Chem. Phys. 47, 335 (1967).
- 16. G. Herzberg, Atomic Spectra and Atomic Structure, Dover Publications, New York (1944), p. 200.
- 17. Y. Baskin, J. Am. Ceram. Soc. 48, 652 (1965).
- C. H. Schramm, P. Gordon, and A. R. Kaufmann, J. of Metals 188, 195 (1950).
- J. L. Margrave, in Physico-Chemical Measurements at High Temperature, J. O'M. Bockris, J. L. White, and J. D. MacKenzie, Eds., Butterworth Scientific Publications, Ltd., London (1959), Chapter 10.
- 20. J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).

SHOP STREET

No. of Competings and P. E. Lee, J. Chee. Phys. (1984).

and the charge and the contract of the contrac

The tradition of the series, too and provide the series and the series of the series and the series of the series

A. Allbert, A. Br Jaminson, and a. C. Chrey, Arear Esergy Research
Larybitionson E. Report, Asses, Chrey, Chrey, Arear Esergy Research

A R. C. Bussen, Los Alemen Strengthe Library (22) mis communication)

The Party of the Control of the Party of the

P. E. G. Buck, R. C. Shitely and R. J. Buck, white-confidence Smither

S. Ha Sonkin and P. D. Sonleis, the hoors, Sage, character, and perfect charge

P. St. W. C. Michel, D. H. Stree, Co. C. Ehrlige, Areas Street Manager.

To a Manual Asia Common Paramet Progress Report, Joseph 1925, 182-1935.

111 ft. C. Karby Sirk Farmer I. Transaction Foundation and antegrater of Commission and Commission of Commission of Commission and Commission of Commiss

114 to A. Chorta, 12 Styre of Diction Compro Report, And Concepts

• Conference 1997, ASD-5186 (Aug 1997), Walls

136 . 3. W. Werning, Chiverstry of California Seliction Laboratory Report, Contract California Seliction Laboratory Report,

AA . A. A. Mader and Chem. Physical Communication of the AA.

15 345. ft. Househilds bleen, Property 325 (1967).

 D. Harmberg, Alberta States and Aborton States are, Dever Publications, New York (1944) ptp. 200.

11. 14 Bestion J. 10. Corner Sec. 151, 652-(1965).

12. C. M. Schrone, P. Guydon, and A. T. Lautinann, J. of No. glas 185, 185, (1959).

1. L. Margravo, 15 Physics - Chemical Versel versel and the Arthur Minestella State of the Arthur Versel Ve

20. L. W. Devos and D. F. Stevensky I. As. Chim. 196. 75, 346 (1956).

- 21. W. Ploch and W. Walcher, Rev. Sci. Instru. 22, 1028 (1951).
- R. J. Ackermann, E. G. Rauh, and M. S. Chandrasekharaiah, A Thermodynamic Study of the Urania-Uranium System, ANL-7048 (July 1965), pp. 24-26.
- D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, Advances in Chemistry Series, No. 18, American Chemical Society (1956).
- 24. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley & Sons, Inc., New York (1963), p. 299.
- J. E. Brugger, in Chemical Engineering Division Research Highlights, May 1965-April 1966, ANL-7175, p. 142.
- 26. P. A. G. O'Hare and W. N. Hubbard, Trans. Faraday Soc. 62, 2709 (1966).
- 27. P. A. G. O'Hare, J. L. Settle, H. M. Feder, and W. N. Hubbard in Thermodynamics of Nuclear Materials, 1967, International Atomic Energy Agency, Vienna (1968), p. 265.
- 28. R. J. Ackermann and E. G. Rauh, J. Phys. Chem., to be published.
- 29. A. Pattoret, J. Drowart, and S. Smoes, paper SM.98/49 in Thermodynamics of Nuclear Materials, 1967 (Proceedings of a Symposium on the Thermodynamics of Nuclear Materials with Emphasis on Solution Systems held by the International Atomic Energy Agency at Vienna, 4-8 September 1967), International Atomic Energy Agency, Vienna (1968), pp. 613-636.
- 30. J. W. Ward, R. N. R. Mulford, and M. Kahn, J. Chem. Phys. 47, 1710 (1967).
- 31. J. M. Leitnaker and T. F. Godfrey, J. Nucl. Mat. 21, 175 (1967).
- 32. E. G. Rauh and R. J. Thorn, J. Chem. Phys. 22, 1414 (1954).

